Dielectric Properties of Water-Oil System Solubilized with Aerosol OT (Physical and Inorganic Chemistry)

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With a view to elucidating the dielectric characteristics of a solubilized system which is different in blending state from both molecular solutions and emulsions, the dielectric constant and the electrical conductivity of solubilized systems of water in kerosine with Aerosol OT were measured over the frequency range of 20 Hz to 5 MHz and the temperature range of 5 to 60°C. The dielectric constant of the solubilized systems examined showed a remarkable dielectric dispersion at frequencies above 100 kHz. At lower frequencies below 30 kHz, the dielectric constant and the conductivity were independent of frequencies, and were different from values expected from theories and experimental information of molecular solutions and emulsions. These limiting values at lower frequencies showed changes in the temperature dependence at 5 : 1, 30 : 1 and 56 : 1 by mole ratio of water to Aerosol OT regardless of the amount of kerosine.

INTRODUCTION

It is known that binary mixtures of liquids show the dielectric behavior characteristic of their blending state.

A molecular solution composed of two liquids miscible with each other shows a dielectric constant which is determined with the composition and is independent of measuring frequency within a frequency range where each constituent liquid shows static dielectric constants and D.C. electrical conductivities.

Contrary to the molecular solution, dielectric constants and conductivities of emulsions, which are heterogeneous mixtures of two liquids immiscible with each other, depend on blending state as well as on composition. Oil-in-water emulsions show dielectric constants and conductivities independent of measuring frequency[1], whereas water-in-oil emulsions show a remarkable dielectric dispersion[2].

A clear conclusion may be drawn from the aforementioned results that a distinct difference in dielectric behavior is found between molecular solutions and emulsions.

From the point of view of blending state, a solubilized system of water in oil and *vice versa* with the aid of appropriate surfactants is of particular interest. In view of the difficulty and the accuracy of dielectric measurement, a solubilized system of water in oil is more preferable to that of oil in water, as the D.C. conductivity is supposed to be lower in the former system than in the latter[3,4].

In the present paper, dielectric constants and conductivities of a solubilized

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system of water in kerosine with Aerosol OT are measured to discuss the dielectric characteristics in the light of theoretical and experimental results for molecular solutions and emulsions.

EXPERIMENTAL

i) Purification of Aerosol OT[5].

Aerosol OT (Sodium dioctyl sulfosuccinate) obtained from American Cyanamid Co. was used throughout the experiment. Ten gms of Aerosol OT was dissolved in 15 mls of dry methanol. The residue of the solution is removed by centrifugation and filtration. The transparent solution was taken to dryness with vacuum pump and by heating with infrared lamp. The final residue is colorless.

ii) Dielectric measurements.

Capacitances and conductances were measured with a transformer bridge over a frequency range of 20 Hz to 5 MHz. A dielectric cell used was composed of coaxial platinum cylinders, the empty capacity being 28.0 $\mu\mu$F.

RESULTS AND DISCUSSION

i) Solubilization of water.

Measurement of solubilization of water was made by means of turbidity observation. Table 1 shows results of solubilization test of Aerosol OT in various solvents. From the results it was found that kerosine showed the maximum ability to solubilize water with a definite amount of Aerosol OT.

Table 1. Solubilization of water in various solvents with Aerosol OT at 25°C. Concentration of Aerosol OT in solvents: 2g./10 mls.

Solvent	Mls. water/gram Aerosol OT
Petroleum ether (b. p. 35-80°C)	0.65
Petroleum benzin	0.65
Ligroin (80-130°C)	0.50
Kerosine (110-250°C)	1.3
Solvent naphtha	0.50
Xylene	0.30
Carbon tetrachloride	0.30
Cyclohexane	0.50
n-dodecane	1.73[a]

[a] See Ref. 6

Figure 1 shows the results of solubilization test of water with Aerosol OT in kerosine. As readily seen in the figure, the amount of solubilized water is approximately proportional to that of Aerosol OT dissolved in kerosine with deviation from the linear relation at concentrations more than about 4 gms Aerosol OT per 10 mls kerosine. The linear relationship implies the presence of some complex of Aerosol OT molecules with water at some definite proportion.

In order to examine the temperature effect, the change in states with temperature was further observed for the specimens which were used to determine the critical solubilization points plotted in Fig. 1. These specimens were transparent below 20°C, being in slightly bluish translucence for lower concentrations of Aerosol OT, whereas above 20°C they changed into opaque state.

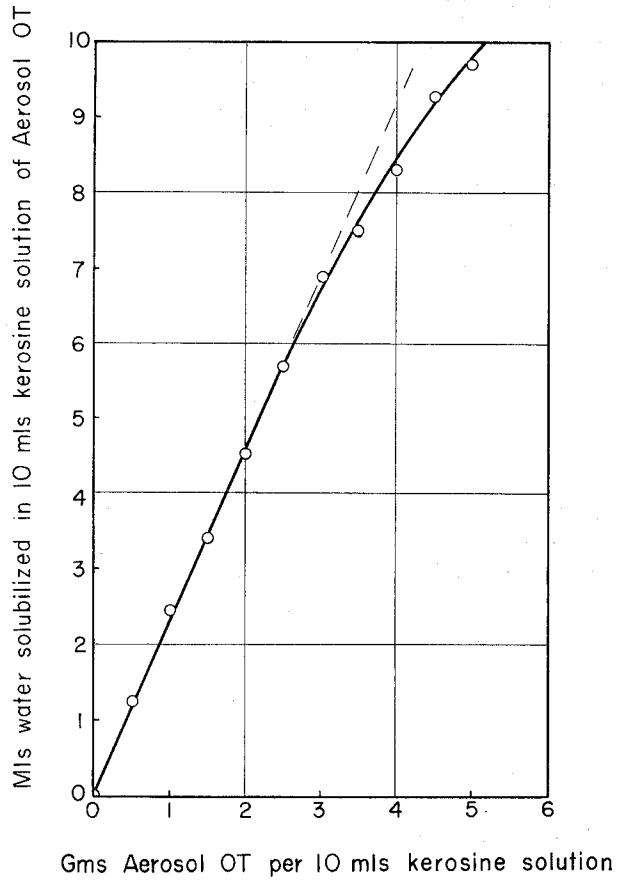

Fig. 1. Solubilization of water in kerosine with Aerosol OT.

ii) Dielectric constants and electrical conductivities of the solubilized systems.

Dielectric measurements were carried out on the specimens with compositions listed in Table 2. These specimens all were in a transparent state within measuring temperature ranges. The dielectric constant and the conductivity of all the specimens showed a remarkable dependence on frequency.

In Fig. 2 is shown a typical example of dielectric constant ε' and conductivity κ (in mho/cm) measured on specimen C4 at varied frequency. The dielectric constant and the conductivity showed values independent of frequency below 30 kHz, and showed a remarkable dielectric dispersion above 100 kHz, Hence, dielectric losses ε'' associated with the dielectric dispersion are calculated with the relation

$$\varepsilon'' = \frac{q}{\omega}(\kappa - \kappa_l),$$

Table 2. Composition of the specimens subjected to dielectric investigation. The oil phases are kerosine solutions of Aerosol OT.

Specimen	Volume fraction of water solubilized in oil phase	Gms Aerosol OT in 10 mls oil phase
A1	0.00	1.5
A2	0.05	
A3	0.10	
A4	0.15	
A5	0.20	
B1	0.00	2.5
B2	0.05	
B3	0.10	
B4	0.15	
B5	0.20	
B6	0.30	
C1	0.00	5.0
C2	0.05	
C3	0.10	
C4	0.15	
C5	0.20	
C6	0.30	
C7	0.40	
C8	0.48	

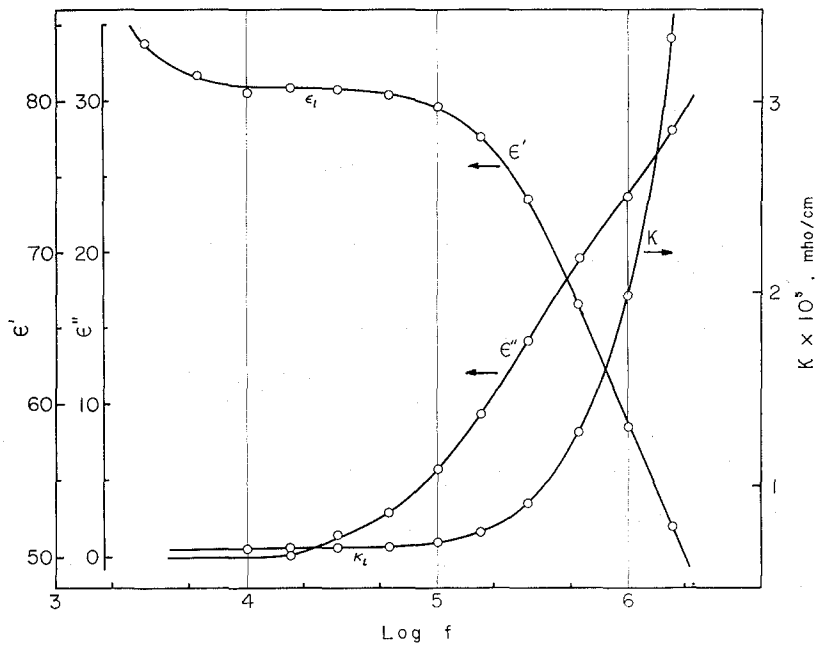

Fig. 2. Frequency dependence of the dielectric constant ε', the conductivity κ and the loss factor ε'' of a solubilized system of water in kerosine with Aerosol OT (specimen C4 in Table 2).

where κ_l is the limiting conductivity at low frequencies, *i.e.* D.C. conductivity, q a numerical factor $q=11.294\times10^{12}$ cm/F, and ω the angular frequency euqal to $2\pi f$. As seen in Fig. 2, the dielectric loss ε'' increases with increasing frequency. Fig. 3 is complex plane plots of the data shown in Fig. 2.

All the specimens measured showed the dielectric behavior similar to that shown in Figs. 2 and 3. Dielectric constants at low frequencies ε_l and limiting conductivities at low frequencies κ_l of each specimen are plotted against temperature in Figs. 4, and 5.

The dielectric behavior of the solubilized system shown in Figs. 4 and 5 may thus be classified into three types:

I) *The system at lower water concentration.*

While the dielectric constant decreases slowly with the increase in temperature, the conductivity increases with temperature. The characteristics are found in the solubilized systems with mole ratios less than 5 : 1 (moles water : mole Aerosol OT). These characteristics are found in most of polar liquids and solutions of polar materials in non-polar solvents.

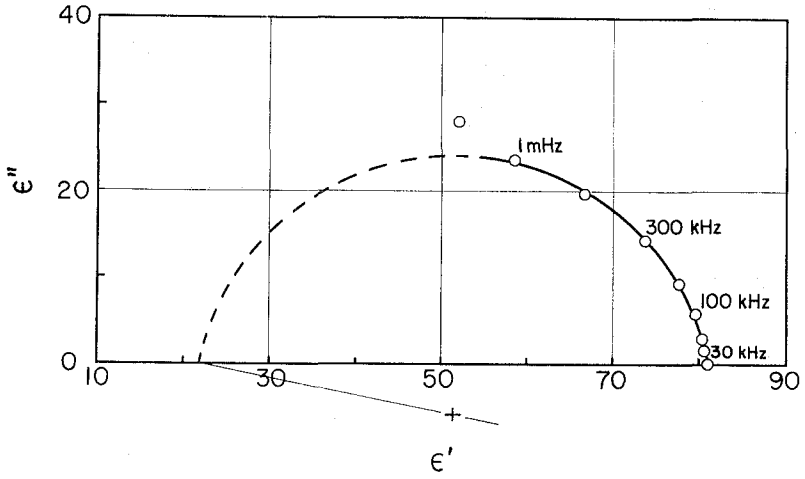

Fig. 3. Complex plane plots of a solubilized system. The same data as given in Fig. 2.

II) *The system at medium water concentration.*

Both the dielectric constant and the conductivity increase slowly with the rise of temperatue for the systems in medium concentrations with mole ratios less than 30 : 1. Such a kind of anomalous behavior is found also for some polar liquids in dimer-association such as acetic acid and butyric acid.

III) *The system at higher water concentration.*

Both the dielectric constant and the conductivity increase abruptly at higher temperatures far beyond the measurable range of the A.C. bridge used. Water molecules can be dissolved to oil phase with a mole ratio up to 56 : 1.

iii) Dielectric constants of dioxane-water mixtures.

In order to compare the data with those of molecular solution, dielectric con-

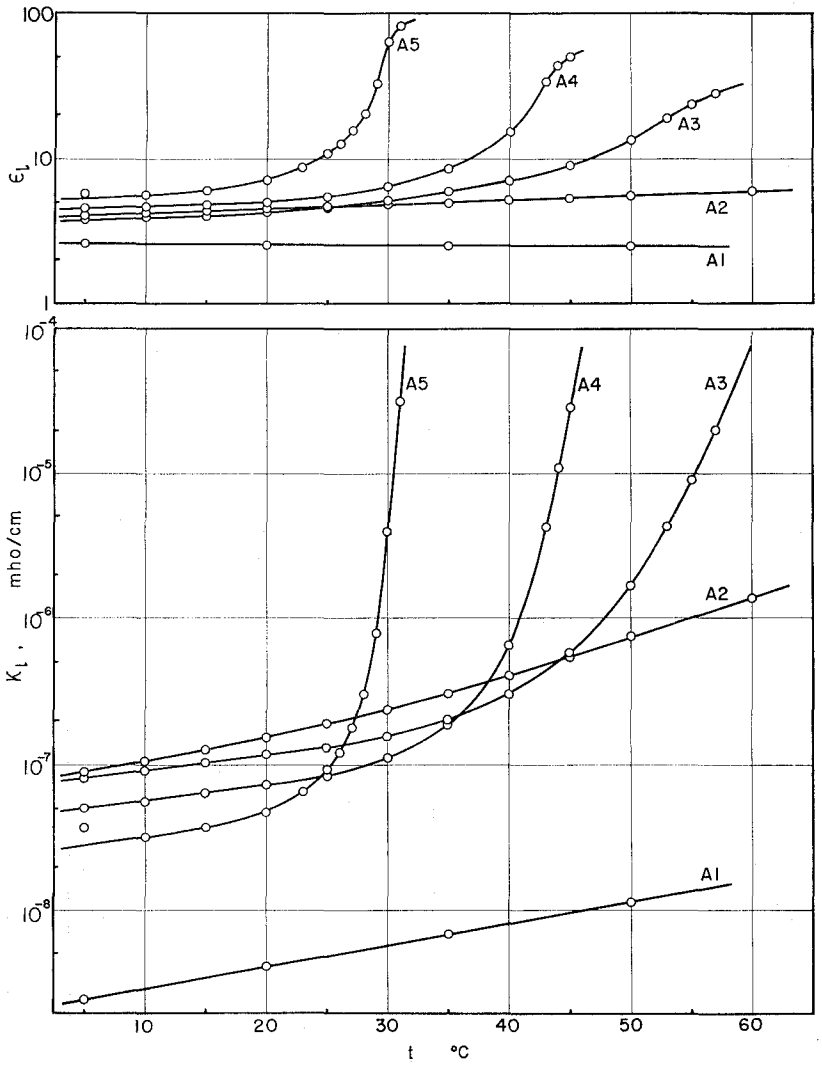

Fig. 4. Temperature dependence of the dielectric constants at low frequencies ε_l and the associated conductivities κ_l for solubilized system given in Table 2. Numbers beside the curves denote the specimens shown in Table 2.

stants of mixtures of distilled water and 1,4-dioxane were measured. The dielectric constants and the conductivities of the mixture showed values independent of measuring frequency, being tabulated in Table 3. The data are in consistent with those reported by Åkerlöf and Short[7].

iv) Comparison of different types of mixtures: Solubilized system, molecular solution and emulsion.

The dielectric constants of the solubilized system at 20°C where they showed comparatively weak dependence on temperature as seen in Figs. 4 and 5 are plotted against the concentration of water in Fig. 6.

For comparison, data of dielectric constants of molecular solutions and emulsions are introduced theoretically as well as experimentally.

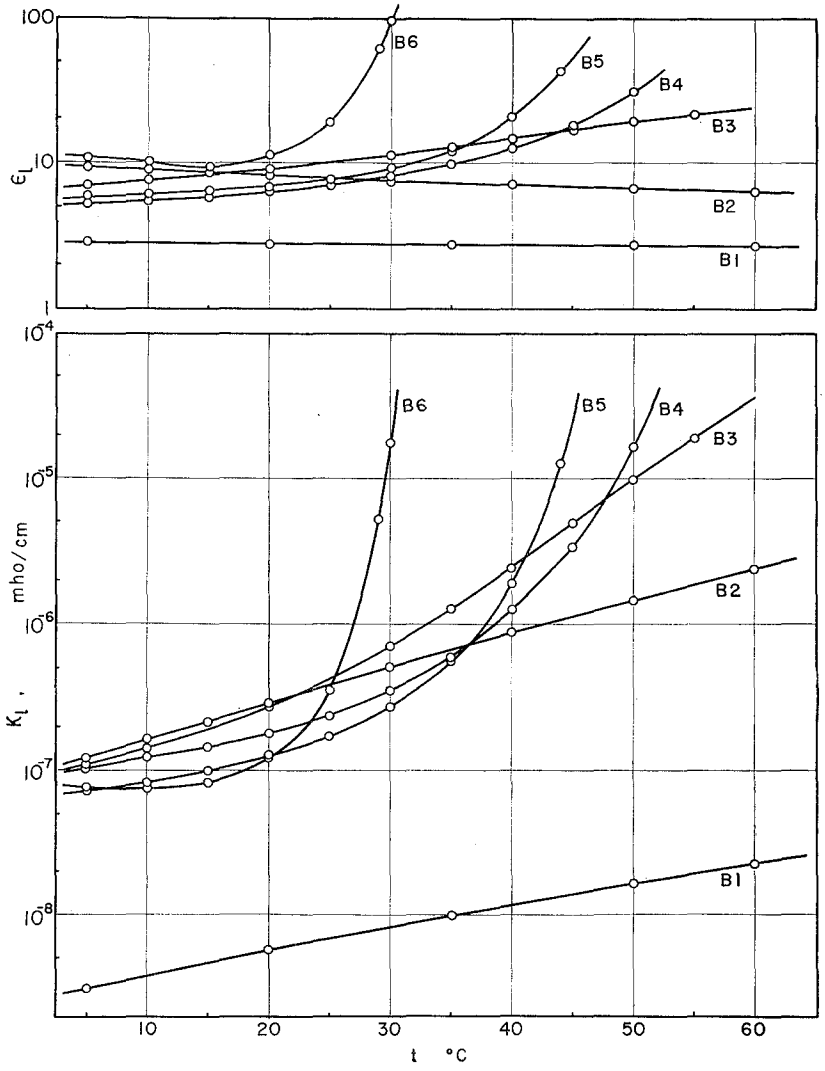

Fig. 5. Temperature dependence of the dielectric constants at low frequencies ε_l and the associated conductivities κ_l for solubilized systems given in Table 2.

According to Onsager's theory dielectric constant ε of a binary mixture consisting of a non-polar liquid a and a polar liquid b is given by

$$\frac{\varepsilon-\varepsilon_a}{2\varepsilon+\varepsilon_a}\Phi_a+\frac{(\varepsilon-\varepsilon_b)(2\varepsilon_b\varepsilon+n_b^4)}{\varepsilon_b(2\varepsilon+n_b^2)^2}\Phi_b=0, \tag{1}$$

where ε_a and ε_b are the dielectric constants of constituent liquids, n_b the refractive index of the polar constituent, and Φ_a and Φ_b the volume fractions of constituents a and b respectively.

Derivation of Eq. 1 is given in Appendix. The theoretical curve of ε against Φ_b by means of Eq. 1 for the water-dioxane system is shown in Fig. 6 together with the measured values given in Table 3.

Next, according to Hanai's dielectric theory[8] of concentrated emulsions, oil-in-

Table 3. Density, specific volume and dielectric constant of water–1, 4-dioxane mixtures at 20°C (30kHz).

Weight % of dioxane	Volume % of dioxane	Density	Specific volume	Dielectric constant
0.00	0.00	0.9983	1.0017	80.55
11.05	10.71	1.0083	0.9918	71.33
22.37	21.77	1.0185	0.9819	61.57
30.76	30.02	1.0252	0.9754	54.14
40.91	40.07	1.0323	0.9687	45.07
50.81	49.94	1.0374	0.9640	36.18
60.89	60.06	1.0405	0.9610	27.38
70.86	70.13	1.0413	0.9603	19.06
80.59	80.04	1.0402	0.9614	11.84
85.19	84.75	1.0390	0.9625	8.890
90.08	89.76	1.0373	0.9640	6.153
95.08	94.92	1.0354	0.9659	3.913
100.00	100.00	1.0336	0.9675	2.216

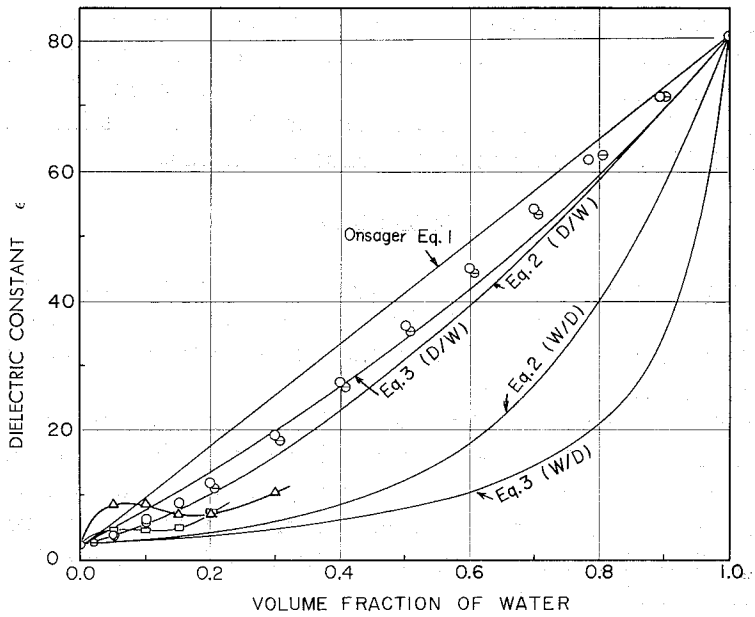

Fig. 6. Comparison of dielectric constants for binary systems in various states of blending.

Theoretical curves:

Onsager Eq. 1, calculated from Eq. 1 by using measured values of dielectric constants and refractive indices for pure dioxane and water;

Eqs. 2 (D/W) and 3(D/W), calculated from Eqs. 2 and 3 respectively provided that globules of dioxane are dispersed in water;

Eqs. 2 (W/D) and 3(W/D), calculated from Eqs. 2 and 3 respectively provided that globules of water are dispersed in dioxane.

Observed values:

○, measured in the present study (Table 3);

⊖, cited from Åkerlöf and Short[7];

△, solubilized systems at 20°C, Fig. 5;

▭, solubilized systems at 20°C, Fig. 4.

water emulsions show too small a dielectric dispersion to be observed in marked contrast with water-in-oil emulsions which are expected to show a remarkable dielectric dispersion. For both emulsions the dielectric constants ε at high frequency are given by

$$\frac{\varepsilon-\varepsilon_p}{\varepsilon_m-\varepsilon_p}\left(\frac{\varepsilon_m}{\varepsilon}\right)^{1/3}=1-\Phi, \tag{2}$$

where subscripts p and m refer to the disperse phase and the continuous medium respectively, and Φ the volume fraction of the disperse phase.

According to Wagner's dielectric theory[9] of dilute emulsions, the dielectric constants ε at high frequencies are given by

$$\varepsilon_h=\varepsilon_m\frac{2\varepsilon_m+\varepsilon_p-2\Phi(\varepsilon_m-\varepsilon_p)}{2\varepsilon_m+\varepsilon_p+\Phi(\varepsilon_m-\varepsilon_p)} \tag{3}$$

for both oil-in-water and water-in-oil emulsions.

In a previous investigation the experimental values for actual emulsions were found to be in better agreement with those given by Eq. 2 than with those by Eq. 3.

Figure 6 shows the comparison between the data on molecular solutions, emulsions and the present solubilized system. From the results it is found that the dielectric constants of the present solubilized system differ from both molecular solution and emulsions, indicating a complex structure in the solubilized system due to Aerosol OT-water complexes or to micelle formation.

CONCLUSIONS

The dielectric behavior of solubilized systems of water in kerosine with Aerosol OT is characteristic of their blending state which is different from both molecular solutions and emulsion. The results imply a particular type of mixture composed of kerosine and Aerosol OT.

A dielectric dispersion was observed in the frequency range above 100 kHz. No decreasing tendency of the loss factor with increasing frequency was observed up to 5 MHz which is the maximum frequency used. The dielectric constants and the conductivities at low frequencies showed changes in the temperature dependence at 5:1, 30:1 and 56:1 by mole ratio of water to Aerosol OT regardless of the amount of kerosine.

APPENDIX

Derivation of Onsager's equation for a binary solution.

According to Onsager[10] the dielectric constant ε of a multicomponent mixture in molecular dispersion is given, on the assumption of additive volumes, by

$$\sum_i\frac{3\varepsilon(\varepsilon-n_i^2)}{2\varepsilon+n_i^2}\Phi_i=4\pi\sum_i N_i\left[\frac{\varepsilon(n_i^2+2)}{2\varepsilon+n_i^2}\right]^2\frac{\mu_i^2}{3kT} \tag{A.1}$$

in which μ, n, Φ and N denote the dipole moment, the refractive index, the volume fraction and the number of molecules in a unit volume of the mixture respectively,

k the Boltzmann constant, T the absolute temperature, and a subscript i refers to molecules or a pure liquid of the ith kind. For a pure liquid with a single component, Eq. A.1 becomes

$$\frac{3\varepsilon_i(\varepsilon_i-n_i^2)}{2\varepsilon_i+n_i^2}=4\pi N_{ip}\left[\frac{\varepsilon_i(n_i^2+2)}{2\varepsilon_i+n_i^2}\right]^2\frac{\mu_i^2}{3kT} \tag{A.2}$$

where N_{ip} means the number of molecules per unit volume of the pure liquid consisting of only the ith kind molecules.

Substituting Eq. A.2 into Eq. A.1 to eliminate μ_i, and using the relation

$$\frac{N_i}{N_{ip}}=\Phi_i \tag{A.3}$$

for additive volumes, we obtain

$$\sum_i\frac{(\varepsilon-\varepsilon_i)(2\varepsilon_i\varepsilon+n_i^4)}{\varepsilon_i(2\varepsilon+n_i^2)^2}\Phi_i=0 \tag{A.4}$$

For a binary system, Eq. A.4 leads to

$$\frac{(\varepsilon-\varepsilon_a)(2\varepsilon_a\varepsilon+n_a^4)}{\varepsilon_a(2\varepsilon+n_a^2)^2}\Phi_a+\frac{(\varepsilon-\varepsilon_b)(2\varepsilon_b\varepsilon+n_b^4)}{\varepsilon_b(2\varepsilon+n_b^2)^2}\Phi_b=0 \tag{A.5}$$

Alternatively we obtain the following expressions

$$\frac{(\varepsilon-\varepsilon_a)(2\varepsilon_a\varepsilon+n_a^4)}{\varepsilon_a(2\varepsilon+n_a^2)^2}\cdot\frac{w_a}{\rho_a}+\frac{(\varepsilon-\varepsilon_b)(2\varepsilon_b\varepsilon+n_b^4)}{\varepsilon_b(2\varepsilon+n_b^2)^2}\cdot\frac{w_b}{\rho_b}=0 \tag{A.6}$$

and

$$\frac{(\varepsilon-\varepsilon_a)(2\varepsilon_a\varepsilon+n_a^4)}{\varepsilon_a(2\varepsilon+n_a^2)^2}\cdot\frac{M_a}{\rho_a}m_a+\frac{(\varepsilon-\varepsilon_b)(2\varepsilon_b\varepsilon+n_b^4)}{\varepsilon_b(2\varepsilon+n_b^2)^2}\cdot\frac{M_b}{\rho_b}m_b=0 \tag{A.7}$$

in terms of weight fraction w_i, mole fraction m_i, molecular weight M_i and density of pure liquids ρ_i.

If the liquid a is non-polar one, Eq. A.5 is simplified with the relation $\varepsilon_a\fallingdotseq n_a^2$ as

$$\frac{\varepsilon-\varepsilon_a}{2\varepsilon+\varepsilon_a}\Phi_a+\frac{(\varepsilon-\varepsilon_b)(2\varepsilon_b\varepsilon+n_b^4)}{\varepsilon_b(2\varepsilon+n_b^2)^2}\Phi_b=0 \tag{A.8}$$

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